Synthesis of sulfonated (ether ether ketone) based membranes containing poly(4-styrenesulfonic acid) and its excellent performance for direct methanol fuel cells

Tao Yang*, Linyan Meng, Ning Huang

School of Chemistry Engineering, Huaihai Institute of Technology, Lianyungang, Jiangsu 222005, China

HIGHLIGHTS

► The blend membranes based on SPEEK and PSSA are prepared.
► The max power density is 28.82 mW cm^{-2} at 100 mA cm^{-2} (2 M methanol, 80 °C).
► A moderate sulfonated PEEK can display excellent performance by doping with PSSA.

GRAPHICAL ABSTRACT
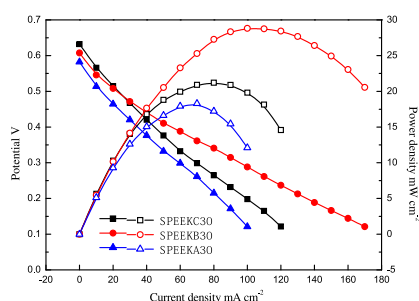
ABSTRACT

A series of blend membranes based on sulfonated poly(ether ether ketone) and poly(4-styrenesulfonic acid) are prepared by solution casting method. The conjunction of the two polymers is evaluated by Fourier Transform Infrared Spectroscopy technique. The thermal stability is determined by Thermogravimetry Analysis. The blend membranes are investigated in terms of swelling behavior, methanol permeability and proton conduction. The Uptake in water and methanol solution distinctly increases with the increasing of the poly(4-styrenesulfonic acid) content. Methanol permeability slightly increases with the increase of the poly(4-styrenesulfonic acid) content and then reaches to a stable value. The proton conductivity is improved with increasing of the poly(4-styrenesulfonic acid) content. The calculated activation energy for proton transportation is ~6 kJ mol^{-1}, which shows that proton can easily conduct through the polymer network. The blend membranes containing 30 wt.% of poly(4-styrenesulfonic acid) are applied in the practical direct methanol fuel cells and their polarization curves with 2.0 mol L^{-1} methanol solution are measured. The max power density is as high as 28.82 mW cm^{-2} at 100 mA cm^{-2} (80 °C). All the results indicate that these membranes based on sulfonated poly(ether ether ketone) and poly(4-styrenesulfonic acid) show good prospect in direct methanol fuel cells.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

1. Introduction

Direct methanol fuel cells (DMFCs) have received much attention due to their advantages such as high energy density, compact structure, environmental friendly, etc [1,2]. During the past decades, much research has been devoted to the investigation of the key components of DMFCs [3,4]. The proton exchange membranes (PEMs) have been extensively studied on the basis of their manifold function [5–11]. PEMs are the crucial part of DMFCs functionally and structurally, which are sandwiched between the anodic and cathodic catalyst layers. PEMs have to separate the fuel and oxidant absolutely and transport the protons through the

* Corresponding author. Tel./fax: +86 518 85895409.
  E-mail address: yangtao_hit@163.com (T. Yang).

membranes easily, in other words, the requirements of high proton conductivity and low methanol permeability have to be fulfilled [7–10]. Traditionally, the high proton conductivity is commonly achieved by the hosted acid groups such as sulfo and carboxyl [12,13]. In Grotthus mechanism, protons transport from one acid ion site to another through the membranes. The mobile H^+ of the acid groups mainly contributes to this proton transportation when the membranes are fully hydrated. The more the acid groups contain in the membranes, the higher the proton conductivity displays. However, it is difficult to obtain low methanol permeability and high proton conductivity simultaneously. It is because that the methanol molecule is too small and the pathways of proton transportation are generally suitable for methanol permeation [13]. Thus, much work has been devoted to the PEMs that own high proton conductivity and low methanol permeability simultaneously [14].

Perghambardoust and Deluca have discussed the classification, fabrication and evaluation of the PEMs materials [5,14]. Perfluorosulfonate ionomer membranes are presently the mostly used PEMs materials because of their high proton conductivity, excellent thermal and chemical stability as well as high mechanical strength when fully hydrated. These advantages are attributed to their C–F backbone chains with many pendant sulfonated exchange sites. However, the rigorous fabrication, high methanol permeability and high cost impede their widespread application in DMFCs and stimulate the investigation on their substitutes [8,9]. Thus, exploring the replacement PEMs with low cost, easy fabrication and high proton conductivity as well as low methanol permeability has become the most vital works for DMFCs [15]. In this regard, the current research emphasis has been shifted to the functionalized non-fluorinated hydrocarbon material and composite membranes [16–20].

Among these non-fluorinated PEMs material, sulfonated poly(-ether ether ketone) (SPEEK) has been considered to be one promising candidate for Nafion membrane. SPEEK presents excellent thermal stability, good chemical resistance and high mechanical properties [21–28]. The desulfonation temperature of SPEEK is reported in the range of 240–330 °C and the degradation of the main chains occurred beyond 450 °C. SPEEK can be easily synthesized via a simple method by sulfonating poly (ether ether ketone) with concentrated sulfuric acid. Another advantage of SPEEK is that the ion exchange capacity (IEC) can be adjusted conveniently by the sulfonating conditions, such as reaction temperature, sulfonation time and the concentration of sulfuric acid. However, high IEC values will usually result in the increase of water uptake and methanol permeability as well as the loss of mechanical strength. To overcome these problems, some inorganic nanoparticles such as montmorillonoid, zeolites, silicon dioxide have been introduced in the SPEEK framework. Inorganic particles are expected to fill in the interstice of the polymer and block the methanol crossover. The performances of thermal stability, mechanical strength and methanol resistance are improved due to the physical properties of these inorganic compounds. However, proton conductivity, the critical attribute of the PEMs, would be reduced because of the physical resistance of these nanoparticles.

Polymer blending is the most frequent method to overcome the respective shortcomings by combining the advantages of the individual components of two or more members. In this regard, many polymers have been blended with SPEEK to obtain the required performance. Swelling ratio can be reduced by blending SPEEK with basic N-containing polymer to generate ionic crosslinking via acid–base interaction at the expense of ionic exchange capacity. In this point of view, poly (benzimidzaole) (PBI) and poly (amide imide) (PAI) were introduced into SPEEK membrane to reduce the methanol permeability and to improve the mechanical strength, however, part of the sulfonic acid groups were inevitably consumed

by the acid–base interaction in the blend system [29–31]. Besides the efforts mentioned above, several investigations have been conducted on the incorporation of polyacrylonitrile (PAN) in SPEEK. The addition of linear PAN has been reported to improve the performance of mechanical strength and methanol permeability. However, the proton conductivity decreased quickly with the increasing of PAN content because of the phase inversion between PAN and SPEEK [32]. Polysulfone (PSF) was also used to reduce the methanol permeability, whereas, phase separation occurred in this blending system [33]. In our previous work, poly(vinyl alcohol) was incorporated into the SPEEK framework to suppress the methanol permeability [34], sulfonated cyclodextrin was used in the SPEEK network as additional proton conductor [35]. A max power density of 29.52 mW cm^{-2} has been achieved at 120 mA cm^{-2} (80 °C).

Presently, the using of the proton conductive additives is regarded as the most prospective recommendation. To enhance the compatibility of the different compositions, the preferred proton conductive additives should have the microstructure similar to that of SPEEK. Poly (4-styrenesulfonic acid) (PSSA), just like SPEEK, has both aromatic ring and proton exchange site of sulfonic group. A similar molecular composition ensures the excellent compatibility between SPEEK and PSSA. Meanwhile, the pendant benzene-sulfonic acid attached to the PSSA backbone displays higher proton conductivity, lower methanol permeability compared to the linear analogues [36]. PSSA has been doped into the inorganic mixture to act as proton conductor [37,38]. PSSA has been blended with alkaline polymer to produce complexation between nitrogen atom and sulfonic groups [39]. PSSA has been widely used as proton conductive additives in PVA network [40–46]. However, the pure PVA exhibits barely proton conduction capacity and the proton transportation is almost performed by the doped PSSA.

In the present work, SPEEK based composite membranes containing poly(4-vinylbenzenesulfonic acid) were prepared. The properties of the blend membranes were investigated as a function of weight fraction of poly(4-vinylbenzenesulfonic acid) in terms of ionic exchange capacity (IEC), water uptake, proton conductivity and methanol permeability in detail. Also displayed was their preliminary usage in DMFC.

2. Experiments

2.1. Materials and membrane preparation

Poly(ether ether ketone) (PEEK, Nanjing Engineering Plastic Ltd., China) was pre-dried at 130 °C overnight. Poly(sodium 4-styrene sulfonated) (Rainful Chemical Co., Ltd., China) was used as received without any treatment.

SPEEK was synthesized by using a modified procedure published elsewhere [35,36]. Firstly, 5 g of PEEK reacted with 250 mL of concentrated sulfonic acid at 50 °C in a round bottom flask. The sulfonation reaction was then terminated by an ice bath after the indicated time of 6 h, 12 h and 48 h, and the as formed SPEEK was denoted as SPEEKA, SPEEKB and SPEEKC, respectively.

The blend membranes were fabricated by using the solution casting method. The indicated amount of SPEEK and poly(sodium 4-styrene sulfonated) were dissolved in N,N-dimethylformamide (DMF) and deionized water, respectively. Both of the two desired solutions were mixed together under speedy stirring. The homogeneous mixture was poured into a glass dish and evaporated at room temperature for 48 h and then annealed at 120 °C for 3 h. The content of PSSA in the blend membranes was controlled as 5, 10, 15, 20, 25 and 30 wt.% with respect to the membranes. The blend membranes as prepared were equilibrated in 0.5 mol L^{-1} H_2SO_4 for 24 h, after washing to the constant pH that were stored in deionized water before the following examinations.

2.2. Characterization methods

FT-IR measurement was performed on a Varian 800 FT-IR spectrometer at the wavenumber range of 4000 down to 400 cm^{-1}. The thermal stability of the blend membranes is analyzed by the TGA technique.

Uptake of the membranes in pure water and methanol solution was measured by using the gravimetric technique. Weight of the wet membranes (W_{wet}) was firstly measured after fully hydrated in deionized water or 2 mol L^{-1} methanol solution at 80 °C, respectively. The dry weight (W_{dry}) was obtained by drying the membranes at 120 °C until constant weight. The water uptake was represented as follows:

$$\text{Uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

Ion exchange capacity (IEC) is assigned to the relative concentration of sulfonic acid groups fixed within the polymer membranes. IEC was determined by the back titration method at 25 °C. The H^{+} forms of the membranes were firstly converted to Na^{+} forms by immersing the membranes in 1 mol L^{-1} NaCl solution by ionic exchange reaction. The released H^{+} was then titrated by 0.01 mol L^{-1} NaOH solution using phenolphthalein as an indicator. The value of IEC was expressed by the following equation:

$$\text{IEC} = \frac{C_{NaOH} \times V_{NaOH}}{W_{dry}} \tag{2}$$

where C_{NaOH} is the molarity of NaOH solution, V_{NaOH} is the consumed mL of NaOH solution, W_{dry} is the weight of dry membranes.

Methanol permeability was evaluated by using the home made diffusion cells. The blend membranes were vertically sandwiched between a receptor (deionized water) and a donor (2.0 mol L^{-1} methanol solution) compartments at 80 °C. Methanol concentration was measured as a function of diffusion time with a GC-17A gas chromatograph (SHIMADZU, Tokyo, Japan). The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{A}{V_B} \times \frac{DK}{L} C_A(t - t_0) \tag{3}$$

where A, L and V_B were the diffusion area, thickness of the membranes and the volume of receptor, respectively. C_A and C_B were the methanol concentration in donor and receptor compartments. DK was the methanol permeability.

Proton conductivity of the blend membranes was measured by the AC impedance technique over the frequency range of 1 Hz to 100 kHz with 5 mV oscillating voltage. The blend membrane was fully hydrated in saturated water vapor at the indicated temperature, which was then sandwiched between two customized stainless-steel electrodes. The impedance measurements were performed on Autolab Electrochemical workstation. The membrane resistance (R) was achieved from the intercept of the impedance fitting curves with the real axis at high frequency. The proton conductivity was calculated as follows:

$$\sigma = \frac{L}{R \times S} \tag{4}$$

L and S were the thickness and the effective area of the membrane.

Selectivity, an index of the relative weight of proton transport in comparison with methanol crossover, is defined as the proton conductivity divided by the methanol permeability.

2.3. MEA fabrication and single cell evaluation

Membrane electrode assembles (MEAs) were fabricated with the blend membranes of SPEEKA30, SPEEKB30 and SPEEKC30. The anode Pt–Ru (Pt: 50%) catalyst loading was 1.0 mg cm^{-2}, and the cathode Pt black loading was 0.5 mg cm^{-2}. The membrane electrode assemble (MEA) with an effective area of 4.0 cm^2 was performed at a pressure of 1 MPa and 130 °C for 150 s. Methanol (2.0 mol L^{-1}) was fed into the anode at a flow rate of 20 mL min^{-1} and oxygen was obtained by the natural air convection at the self-breathing cathode.

3. Results and discussion

3.1. FT-IR absorption spectra and thermal analysis of the blend membranes

The characteristic absorptions of the SPEEK based membranes from 1800 to 800 cm^{-1} are shown in Fig. 1. The absorption at 1652 cm^{-1} is assigned to the carbonyl band, and the two absorptions at 1597 and 1491 cm^{-1} are attributed to the aromatic ring. The speak at 1242 cm^{-1} corresponds to the Ar–O–Ar in SPEEK [34,35], which becomes indistinguishable in presence of PSSA. The absorptions at 1078 and 1024 cm^{-1} are due to the sulfonic acid group [34–36,38,44,45]. The absorptions at 1597, 1078 and 1024 cm^{-1} are enhanced increasingly with the increase of the PSSA content. These characteristic absorptions demonstrate that PSSA has been successfully incorporated in the SPEEK framework.

The thermal stability of the blend membranes are analyzed by the TGA technique and the TGA curves are displayed in Fig. 2. The excellent thermal stability of SPEEK has been published elsewhere [18–22]. All the samples exhibit three dominant degradation steps from room temperature to 700 °C. The first weight loss (less than 10 wt.%) below 100 °C can be assigned to the evaporation of weakly physical and chemical absorbed water in the polymer network. The distinct degradation from 250 to 370 °C is due to the loss of sulfonic acid groups. The weight change occurs at around 450–550 °C represents the thermal decomposition of the main chains of SPEEK and PSSA [24,42]. PSSA is less stable than SPEEK evidenced by the negative shift of onset decomposition temperature. Although the introduction of PSSA reduces the thermal stability of SPEEK membranes, the blend membranes are still stable enough to operate in DMFCs [5,14].
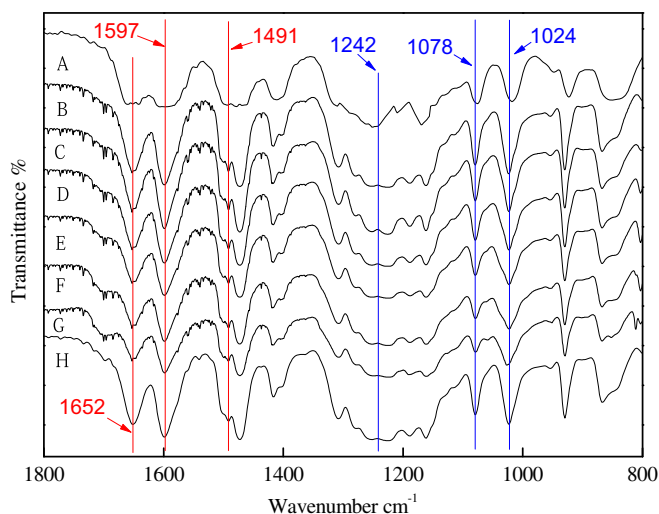

Fig. 1. FTIR spectra of SPEEK based membranes. (A) SPEEKB0, (B) SPEEKB5, (C) SPEEKB10, (D) SPEEKB15, (E) SPEEKB20, (F) SPEEKB25, (G) SPEEKB30, (H) pure PSSA.
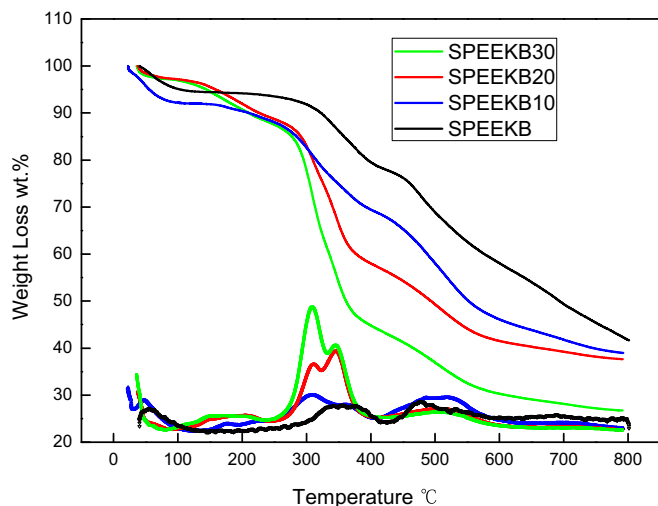
Fig. 2. TGA curves of the SPEEK based membranes.

Fig. 3. Uptake of the SPEEK based membranes as function of PSSA content in water (a) and in 2 mol L^{-1} methanol solution (b).

Fig. 4. IEC of the SPEEK based membranes as function of PSSA content.

3.2. Uptake of the blend membranes in pure water and methanol solution

Uptake plays a leading role in the performance of a proton conductive membrane. Water can influence the microstructure and mechanical properties of the blend membranes, and can also assist the transport of H$^+$, along with the methanol molecule, through the membrane [3,4]. High water uptake commonly contributes to high proton conductivity; at the same time, it is also a sign of low dimensional stability and high methanol permeability. The rigid aromatic ring of SPEEK is responsible for its compact microstructure and high dimensional stability [34,35]. The water uptake of pure SPEEK membrane and blend membranes with various contents of PSSA at 80 °C is shown in Fig. 3. The results show that water uptake increases with the increasing of sulfonation degree [34]. We can also see that the water uptake of the blend membranes increases with increasing the content of PSSA. This may be due to the additional hydrophilic sulfonic groups of PSSA. It has been confirmed that the incorporation of sulfonic groups can increase the hydrophilic property and water absorbability of the polymer matrix [46]. The uptake of SPEEK based membranes in methanol solution is also measured and exhibited in Fig. 3. The membranes in methanol solution show similar uptake behavior to that in pure water.

3.3. Ionic exchange capacity (IEC) of the blend membranes

IEC, the ion exchange capacity of the proton conductive membranes, is defined as the fixed milliequivalents of sulfonic groups per gram of polymer. Proton conductivity commonly increases with increasing the relative concentration of sulfonic group of the polymer [12,13]. However, too many sulfonic groups will reduce the chemical stability of the membranes as well as the resistance to methanol crossover [34,35]. IEC of the pure SPEEK membrane and blend membranes are determined by titration method and the results are shown in Fig. 4. It is noticed that the addition of PSSA can enhance the ion exchange capacity of the blend membranes effectively. It is because that the theoretical ion exchange capacity of PSSA (5.4 mmol g^{-1}) is much higher than that of the synthesized SPEEK. The highest IEC of SPEEK in our work is 2.42 mmol g^{-1}, which is not more than half of the theoretical IEC of PSSA.
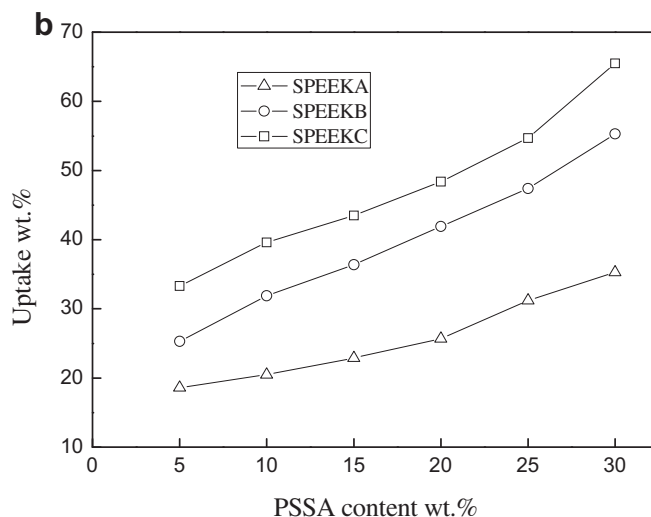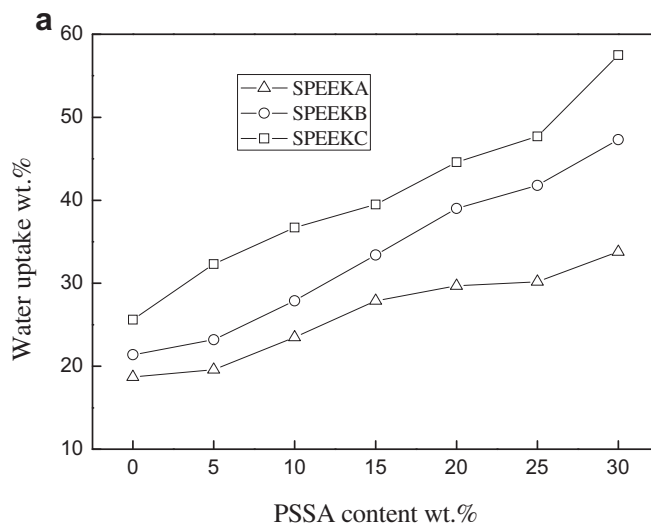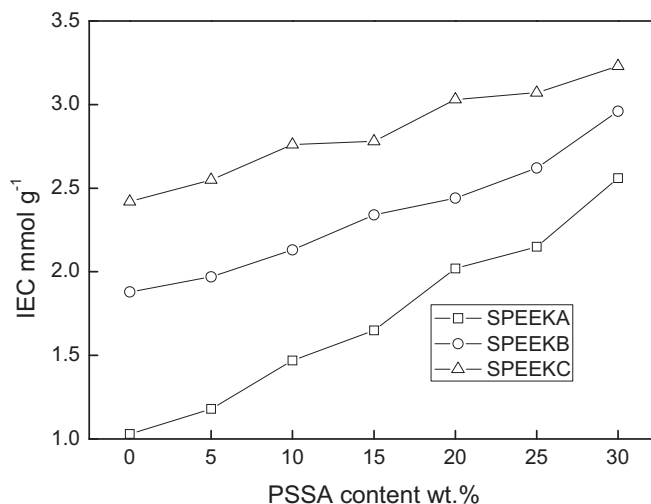
3.4. Methanol permeability and proton conductivity of the blend membranes

Methanol crossover is a boring problem because of its detrimental effect by reducing the Coulombic efficiency [4–11]. The methanol permeability is measured at the methanol concentration of 2.0 mol L^{-1} and 80 °C, the results are shown in Fig. 5. We can see that the methanol permeability increases gradually when the content of PSSA is below 10 wt.%, then reaches to a stable value as the PSSA content is above 20 wt.%. It might because that a little amount of PSSA (below 10 wt.%) cannot form the compact polymer network [39,40]. The final stable permeability value is higher than that of the pure SPEEK. It implies that PSSA, the pendant aromatic network, displays less methanol resistance than SPEEK.

Proton conductivity is the crucial attribute for the proton conductive membrane. It depends heavily on the water uptake and ion exchange capacity. The influence of PSSA on proton conduction is analyzed and demonstrated in Fig. 6. The production conductivity of the blend membranes increases when the content of PSSA increases. The relationship between proton conductivity and temperature follows the Arrhenius equation approximatively in the experimental temperature range of 25–80 °C.

The activation energy for proton transfer can be calculated by the equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where k is Boltzmann constant, E_a is the activation energy of proton conduction, which has been calculated from the slope of $\ln(\sigma)$ versus $1/T$ plots. All the membranes exhibit activation energy not more than 6 kJ mol^{-1}. According to the calculated activation energy in our experiments, both Grotthus mechanism and vehicle mechanism might contribute to the proton transportation in the blend membranes.

The productive membranes owning high proton conductivity generally display high methanol permeability because that the pathways for proton transport might also allow the methanol permeation. A high selectivity implies that the membranes possess both high proton conductivity and low methanol permeability, which is greatly desired in DMFC application [14]. The selectivity of the blend membranes at 80 °C is shown in Fig. 7. The selectivity increases with the increasing of PSSA content, which is highly in agreement with the IEC and methanol permeability test. In our
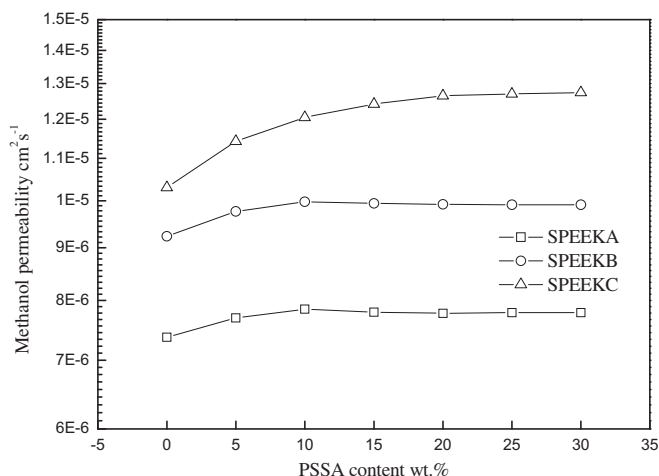
Fig. 5. Methanol permeability of the blend membranes at their indicated compositions and 80 °C.
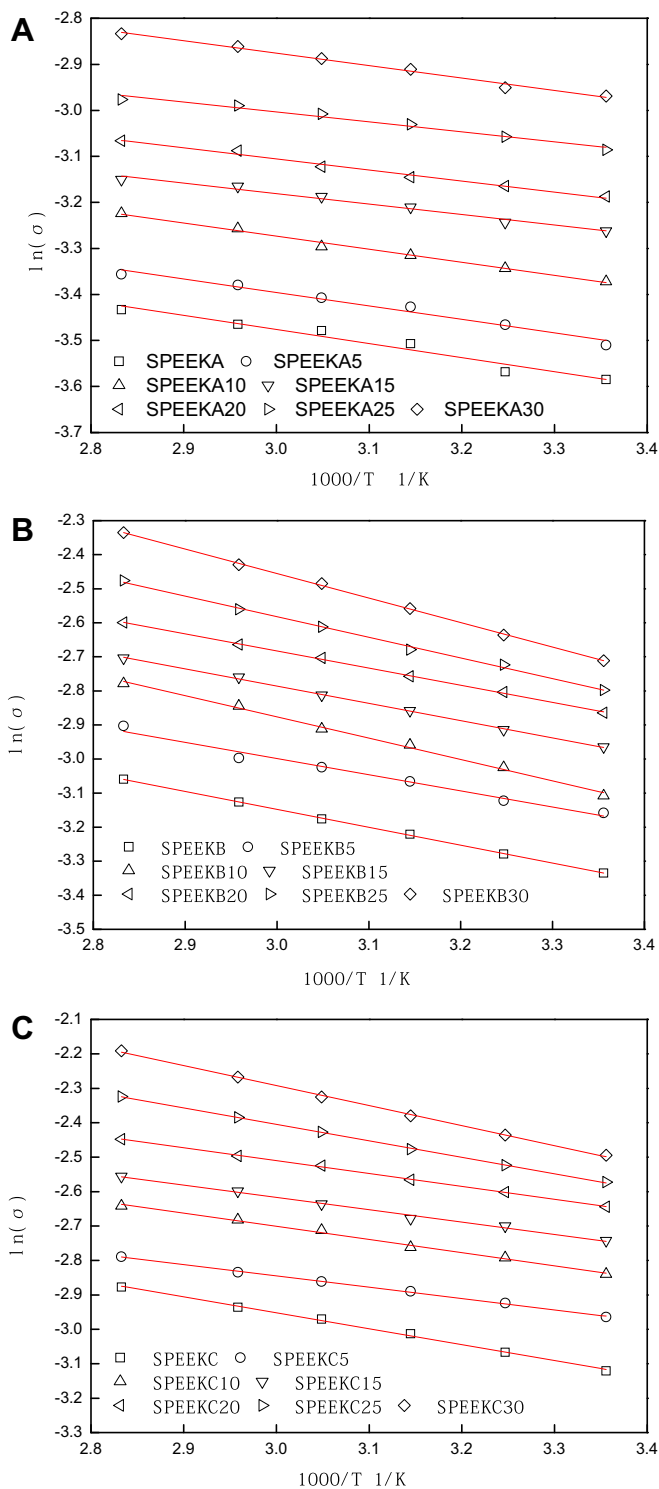
Fig. 6. Proton conductivity of the blend membranes (A) SPEEKA, (B) SPEEKB and (C) SPEEKC as function of operating temperature.

experiments, SPEEKB obtained the highest selectivity than SPEEKA and SPEEKC. Just as mentioned above, selectivity value is the compromise of proton conductivity and methanol permeability.

3.5. MEA testing in a single fuel cell

The evaluation of electrochemical performance under relevant fuel cell conductions is the most straightforward approach to
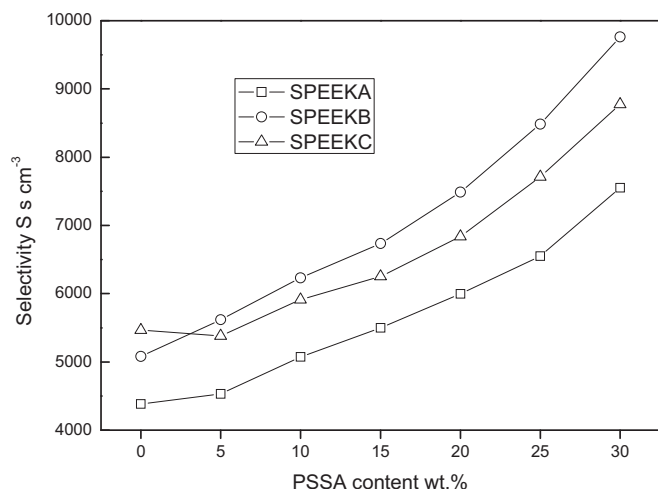
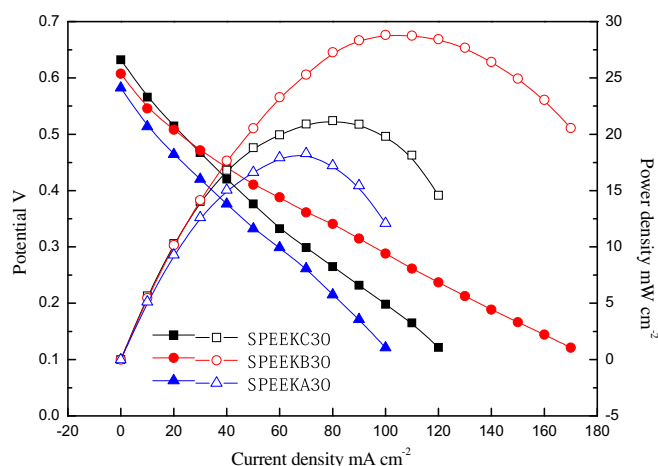**Fig. 7.** Selectivity of the SPEEK based membranes as function of PSSA content.

Fig. 8. Polarization and power density of the MEA with different membranes.

DMFCs application reflected by TGA analysis. The methanol permeability and proton conductivity are both increased by the introduction of PSSA. However, the highest selectivity and power density are achieved by SPEEKB (IEC: 1.88). These results indicate that SPEEK with a moderate sulfonation degree can exhibit excellent performance by doping with PSSA. The optimal composition and the more suitable fabrication of the blend membranes deserve the further investigation.

evaluate a productive membrane. The MEA performance of SPEEKA30, SPEEKB30 and SPEEKC30 is shown in Fig. 8. SPEEKB30 presents the better performance than the other membranes, and the maximum power density is 28.82 mW at the current density of 100 mA cm^{-2}, which is 57.5% and 35.8% higher than the maximum value of SPEEKA30 and SPEEKC30. Compares to SPEEKA30, SPEEKB30 displays the increments of 27.3% and 63.5% in methanol permeability and proton conductivity. When it comes to SPEEKC30, it exhibits the increments of 28.55% and 15.55% in methanol permeability and proton transportation relative to SPEEKB30. In Yang's reports, the PVA/PSSA composite membranes obtained a power density of 23.72 mW cm^{-2} at 148.1 mA cm^{-2} (2 mol L^{-1} methanol, 25 °C) [41,43].

4. Conclusion

The research work on proton conductive membrane replacement is most important to DMFCs. Exploring the suitable modification method is vital for SPEEK membranes application. We report here the synthesis and performance of the blend membranes based on SPEEK and PSSA, also presented is their practical application in DMFCs. The blend membranes are produced by solution casting method conveniently. The compatibility of the two polymers is confirmed by FT-IR spectra. The thermal stability is enough for

References

[1] M. Winter, R.J. Brodd, Chem. Rev. 104 (2004) 4245—4269.
[2] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, J. Power Sources 117 (2003) 22—25.
[3] Y. Shao, G. Yin, Z. Wang, Y. Gao, J. Power Sources 167 (2007) 235—242.
[4] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, J. Power Sources 163 (2007) 743—754.
[5] N.W. Deluca, Y.A. Elabd, J. Polym. Sci., Part B: Polym. Phys. 44 (2006) 2201—2225.
[6] R. Jiang, D. Chu, Electrochem. Solid-State Lett. 5 (2002) A156—A159.
[7] F. Meier, J. Kerres, G. Eigenberger, J. Membr. Sci. 241 (2004) 137—141.
[8] A. Casalegno, R. Marchesi, J. Power Sources 185 (2008) 318—330.
[9] C.Y. Du, T.S. Zhao, W.W. Yang, Electrochim. Acta 52 (2007) 5266—5271.
[10] V. Baglio, A.S. Aricò, V. Antonucci, I. Nicotera, C. Oliviero, L. Coppola, J. Power Sources 163 (2006) 52—55.
[11] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29—39.
[12] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463—1502.
[13] B. Ruffmann, H. Silva, B. Schulte, S.P. Nunes, Solid State Ionics 162—163 (2003) 269—275.
[14] S.J. Perghambardoust, S. Rowshanzamir, M. Amjadi, Int. J. Hydrogen Energy 35 (2010) 9349—9384.
[15] K. Lee, J.D. Nam, J. Power Sources 157 (2006) 201—206.
[16] X. Tongwen, J. Membr. Sci. 263 (2005) 1—29.
[17] H. Tomoya, M. Kazuya, U. Mitsuru, Polymer 50 (2009) 5341—5357.
[18] J.K. Lee, W. Li, A. Manthiram, J. Membr. Sci. 330 (2009) 73—79.
[19] T.H. Young, H.L. Chang, S.P. Hyung, A.M. Kyung, J.K. Hyung, Y.N. Sang, et al., J. Power Sources 175 (2008) 724—731.
[20] W. Sheng, G. Chunli, T.C. Wen, S.C. Yao, C.T. Fang, Int. J. Hydrogen Energy 34 (2009) 8982—8991.
[21] P. Kalappa, J.H. Lee, Polym. Int. 56 (2007) 371—375.
[22] E. Sengul, H. Erdener, A.R. Gultekin, H. Yucel, N. Bac, I. Eroglu, Int. J. Hydrogen Energy 34 (2009) 4645—4652.
[23] B.P. Tripathi, M. Kumar, V.K. Shahi, J. Membr. Sci. 327 (2009) 145—154.
[24] A. Carbone, A. Sacca, I. Gatto, R. Pedicini, E. Passalacqua, Int. J. Hydrogen Energy 33 (2008) 3153—3158.
[25] Y.H. Su, Y.L. Liu, Y.M. Sun, J.Y. Lai, D.M. Wang, Y. Gaoe, et al., J. Membr. Sci. 296 (2007) 21—28.
[26] A.R. Tan, L.M. Carvalho, F.G. Ramos, A.S. Gomes, Macromol. Symp. 245 (2006) 470—475.
[27] Z.W. Gao, Z. Zhen, J. Membr. Sci. 261 (2005) 107—113.
[28] C.S. Karthikeyan, S.P. Nunes, L.A.S.A. Prado, M.L. Ponce, H. Silva, B. Ruffmann, et al., J. Membr. Sci. 254 (2005) 139—146.
[29] H. Zhang, X. Li, C. Zhao, Z. Fu, Y. Shi, H. Na, J. Membr. Sci. 308 (2008) 66—74.
[30] H.L. Wu, C.C.M. Ma, C.H. Li, T.M. Lee, C.Y. Chen, C.L. Chiang, et al., J. Membr. Sci. 280 (2006) 501—508.
[31] C. Zhao, Z. Wang, D. Bi, H. Lin, K. Shao, T. Fu, S. Zhong, H. Na, Polymer 48 (2007) 3090—3097.
[32] J. Wang, Z. Yue, J. Economy, J. Membr. Sci. 291 (2007) 210—219.
[33] F. Lufrano, G. Squadrito, J. Appl. Polym. Sci. 77 (2000) 1250—1256.
[34] T. Yang, Q. Xu, Y. Wang, B. Lu, P. Zhang, Int. J. Hydrogen Energy 33 (2008) 6766—6771.
[35] T. Yang, C. liu, Int. J. Hydrogen Energy 36 (2011) 5666—5674.
[36] Y.H. Su, Y.L. Liu, D.M. Wang, J.Y. Lai, Y.M. Sun, S.D. Chyou, W.T. Lee, J. Membr. Sci. 349 (2010) 244—250.
[37] K. Fatyeyeva, J. Bigarré, B. Blondel, H. Galiano, D. Gaud, M. Lecardeur, F. Poncin-Epaillar, J. Membr. Sci. 366 (2011) 33—42.
[38] K.T. Park, S.G. Kim, J.H. Chun, D.H. Jo, B.H. Chun, W.I. Jang, G.B. Kang, S.H. Kim, K.B. Lee, Int. J. Hydrogen Energy 36 (2011) 10891—10900.
[39] O. Acar, U. Sen, A. Bozkurt, A. Ata, J. Mater. Sci. 45 (2010) 993—998.
[40] Jin Ah Seo, Joo Hwan Koh, Dong Kyu Roh, Jong Hak Kim, Solid State Ionics 180 (2009) 998—1002.

[41] C.C. Yang, Int. J. Hydrogen Energy 36 (2011) 4419−4431.
[42] A.K. Sahu, G. Selvarani, S.D. Bhat, S. Pitchumani, P. Sridhar, A.K. Shukla, N. Narayanan, A. Banerjee, N. Chandrakumar, J. Membr. Sci. 319 (2008) 298−305.
[43] C.C. Yang, W.C. Chien, Y.J. Li, J. Power Sources 195 (2010) 3407−3415.

[44] C.W. Lin, Y.F. Huang, A.M. Kannan, J. Power Sources 164 (2007) 449−456.
[45] D.S. Kim, M.D. Guiver, S.Y. Nam, T.I. Yun, M.Y. Seo, S.J. Kim, H.S. Hwang, J.W. Rhim, J. Membr. Sci. 281 (2006) 156−162.
[46] D.S. Kim, H.I. Cho, D.H. Kim, B.S. Lee, B.S. Lee, S.W. Yoon, Y.S. Kim, G.Y. Moon, H. Byun, J.W. Rhim, J. Membr. Sci. 342 (2009) 138−144.